

Recent Developments in Autothermal Reforming and Prereforming for Synthesis Gas Production in GTL Applications

Kim Aasberg-Petersen*, Thomas S. Christensen,
Charlotte Stub Nielsen, Ib Dybkjær

Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark

Introduction

Processes for conversion of natural gas into liquid fuels ("Gas-to-Liquids" or GTL) such as gasoline or diesel produced by Fischer-Tropsch (FT) synthesis are attracting increased attention. A GTL-plant for production of FT-products can be divided into three sections. In the first section, the natural gas is converted into synthesis gas – a mixture of hydrogen and carbon oxides. In the second part, the actual FT synthesis takes place and in the final section, product upgrading and separation occurs.

The most capital-intensive part of the GTL-plant is the preparation of synthesis gas, which may account for 50-75% of the capital cost [1]. Hence, there is a considerable incentive to optimise technologies for reducing the cost. Autothermal Reforming (ATR) has been identified as the preferred option for large-scale safe and economic synthesis gas production. This paper will focus on recent developments in the prereforming and ATR technology for synthesis gas production.

Process Concepts and Synthesis Gas Composition

A typical process concept for production of synthesis gas based on ATR is shown in Figure 1. The key steps in the process scheme are desulphurisation, adiabatic prereforming, autothermal reforming, and heat recovery.

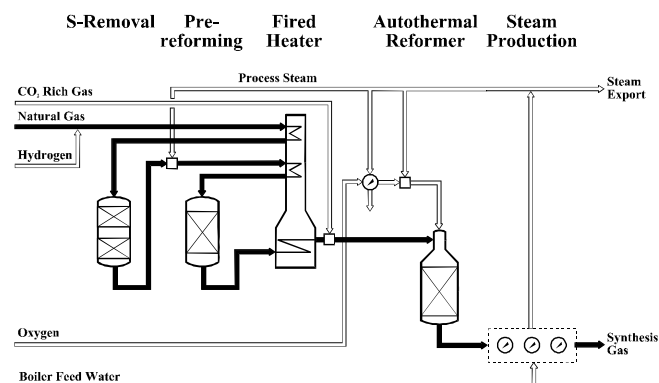


Figure 1. Process Concept for Synthesis Gas Production by Adiabatic Prereforming and Autothermal Reforming

The desired exit gas composition for most FT-applications is an H_2/CO -ratio of about 2. This ratio is achieved by recirculating CO_2 . Reducing the amount of steam added to the hydrocarbon feedstock decreases the H_2/CO -ratio and the required recirculation of carbon dioxide. Operation at low steam-to-carbon (H_2O/C) ratio improves process economics, as illustrated in Table 1 [1]. Operation at H_2O/C -ratios of 0.6 has been proven industrially [3] and large-scale GTL projects for production of FT-fuels based on ATR have been publicized [4].

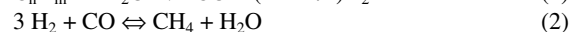
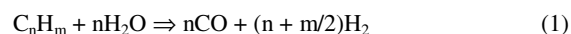
Table 1. Process Economics with Various H_2O/C -Ratios [1]

| H_2O/C | 0.2 | 0.6 | 1.0 |
|-----------------------------|------|------|------|
| Relative Energy Consumption | 0.97 | 1.00 | 1.03 |
| Relative Investment | 0.9 | 1.0 | 1.1 |

The Air Separation Unit (ASU) for production of pure oxygen accounts for a large part of the investment of the production of synthesis gas. The use of a prereformer in the process scheme in Figure 1 upstream the ATR reactor reduces the oxygen consumption per unit of product produced.

Prereforming and ATR at Low H_2O/C -ratios

In the prereformer, all higher hydrocarbons (C_{2+}) are converted into a mixture of methane, hydrogen, and carbon oxides according to the following reactions:



The prereformer is an adiabatic fixed-bed reactor with highly active nickel catalysts.

The ATR reactor consists of a burner, a combustion chamber, and a fixed bed catalyst section contained in a refractory lined pressure shell [2]. The key elements in the ATR reactor is the burner and the catalyst bed [2]. The burner provides mixing of the feed streams and the natural gas is converted in a turbulent diffusion flame often simplified by the following reaction:



The catalyst bed equilibrates the methane steam reforming (reverse of (2)) and the shift (3) reactions.

As shown in Table 1, there is a considerable economic incentive to reduce the H_2O/C -ratio in a GTL plant. However, operation with low H_2O/C -ratios involves the risk of soot formation in the ATR reactor and whisker carbon formation in the prereformer. In order to overcome this challenge, both fundamental studies and extensive pilot plant operation have been carried out to understand and push the limits towards lower H_2O/C -ratios.

In a prereformer, whisker carbon can be formed either from methane or higher hydrocarbons. The lower limit of the H_2O/C -ratio depends on a number of factors including the feed gas composition, the operating temperature and the choice of catalyst. In a prereformer operating at low H_2O/C -ratio, the risk of carbon formation [5] from methane is most pronounced in the reaction zone where the temperature is highest. Carbon formation from higher hydrocarbons can only take place in the first part of the reactor with the highest concentrations of C_{2+} compounds. In Figure 2, a measured temperature profile from a prereformer pilot plant run operating at an H_2O/C -ratio of 0.4 is presented. Post-test analysis of the catalyst showed that no carbon formation had occurred.

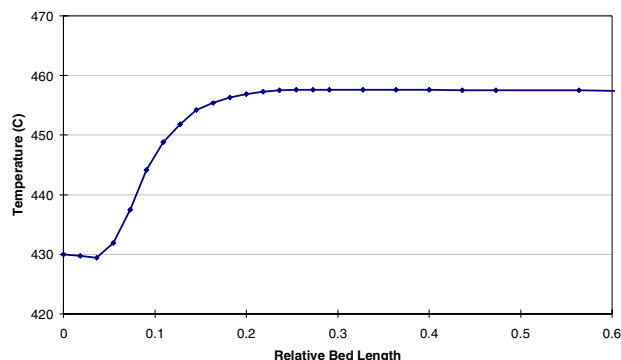


Figure 2. Temperature profile in Adiabatic Prereformer during pilot plant operation. $H_2O/C = 0.4$.

The risk of soot formation in an ATR reactor depends on a number of parameters including feed gas composition, temperature, pressure, and especially burner design. Soot precursors may be formed in the combustion chamber during operation. It is essential that the design of burner, catalyst and reactor is such that the precursors are destroyed by the catalyst bed to avoid soot formation. In Table 2, examples of operating conditions without soot formation in a pilot plant are given [2].

Table 2: Autothermal Reforming - Pilot Plant Demonstration Runs at Low H_2O/C -Ratios [2]

| Test | A | B |
|---------------------------------------|------|------|
| Feed Ratios ¹⁾ (mole/mole) | | |
| H_2O/C | 0.60 | 0.36 |
| O_2/C ²⁾ | 0.58 | 0.57 |
| Product Gas | | |
| Temperature, (°C) | 1020 | 1022 |
| Pressure, (bar) | 28.5 | 28.5 |
| H_2/CO , (mole/mole) | 2.30 | 2.15 |
| Total run hours | 2235 | 920 |

Notes: 1) Mole per mole of hydrocarbon C-atoms
 2) The O_2/C -ratio is approximately 5% higher than truly adiabatic reactors with same exit temperature.

Conclusion

The combination of adiabatic prereforming and autothermal reforming at low H_2O/C -ratios is a preferred layout for production of synthesis gas for large GTL-plants. Extensive testing and demonstration in pilot plants have proven that the technologies are ready for application in large industrial scale.

References

- [1] Dybkjær, I. and Christensen, T.S., *Stud. Surf. Sci. Catal.*, 136 (2001) 435.
- [2] Christensen, T.S.; Østberg, M.; and Bak Hansen, J.-H., "Process Demonstration of Autothermal Reforming at Low Steam-to-Carbon Ratios for Production of Synthesis Gas", *AIChE Annual Meeting*, Reno, USA, Nov. 4-9, 2001
- [3] Ernst, W.S.; Venables, S.C.; Christensen, P.S.; and Berthelsen, A.C., *Hydrocarbon Proc.*, 79(3) (2000), 100-C

- [4] Rostrup-Nielsen, J.R.; Dybkjær, I.; and Coulthard, G.R.G., "Synthesis Gas for Large-Scale GTL-Plants", *AIChE Spring Annual Meeting*, Houston, USA, April 22-26, 2001
- [5] Rostrup-Nielsen, J.R. and Sehested, J., *Stud. Surf. Sci. Catal.*, 139 (2001) 1.